Type I band alignment in the GaN_xAs_{1-x}/GaAs quantum wells

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(Received 27 July 2000; revised manuscript received 22 September 2000; published 28 December 2000)

Three independent experimental techniques, namely, time-resolved photoluminescence (PL) spectroscopy, PL polarization, and optically detected cyclotron resonance, are employed to determine the band alignment of GaN_xAs_{1-x}/GaAs quantum structures with a low-N composition. It is concluded that band lineup is type I based on the following experimental results: (i) comparable radiative decay time of the GaNAs-related emission measured from single GaNAs epilayers and from GaNAs/GaAs quantum well (QW) structures; (ii) polarization of the GaNAs-related emission; and (iii) spatial confinement of the photoexcited holes within the GaNAs layers under resonant excitation of the GaNAs QW's.

DOI: 10.1103/PhysRevB.63.033303 PACS number(s): 71.20.Nr, 78.47.+p, 78.66.Fd, 76.40.+b

Nitrogen-containing III-V-V′ alloys and related quantum structures have been extensively investigated[1–8] in recent years owing to their great scientific interest as well as their technological importance for optoelectronics and photonics. One of the remaining unsolved issues regarding the electronic properties of GaNAs/GaAs quantum structures involves the band edge alignment. Although it is commonly accepted that the bowing in the GaNAs band gap energy occurs mainly due to the lowering of the conduction band (CB) edge, leading to a large CB offset and only a small discontinuity in the valence band (VB) edge,[7,8] an in-depth understanding is so far still lacking even regarding the fundamental type of the band alignment as type I or II. Early theoretical studies based on the dielectric model predicted type II alignment for the GaNAs/GaAs system.[1] In contrast, more recent first-principles calculations suggest a type I lineup in the system.[2] The only experimental results available so far, obtained using x-ray photoemission spectroscopy, favored the type II band lineup.[7] However, the large error bar of the experimental data, which essentially exceeds the values of the VB offset obtained, casts doubt on the reliability of this conclusion. This is unfortunate, since information about band alignment is not only important for possible device applications, but also valuable in examining the validity of the approximations made in theoretical models and thus in understanding the fundamental band structure of the nitrogen-containing III-V-N alloys.

In this paper we shall provide direct experimental evidence that the band alignment in GaN_xAs_{1-x}/GaAs heterostructures with N content up to 3.3% is, in fact, type I. This conclusion is based on the results obtained by using three different experimental techniques, namely, time-resolved photoluminescence (PL) spectroscopy, PL polarization measurements, and optically detected cyclotron resonance (ODCR) studies.

Two types of sample structure were used in this study; all samples were grown by gas source molecular beam epitaxy (MBE) on semi-insulating GaAs substrates. The first type is GaNAs/GaAs multiple quantum well (MQW) structures consisting of seven periods of 70-Å-thick GaN_xAs_{1-x} QW's placed between 200-Å-thick GaAs barriers. The second type of sample structure is single 1100-Å-thick strained GaN_xAs_{1-x} epilayers. All samples are undoped and were grown with a 100-Å-thick GaAs cap layer and a 2500-Å-thick GaAs buffer. The N composition x in the structures was varied from 1.1% up to 3.3%. PL was excited by a tunable, cw Ti:sapphire solid state laser and detected through a double-grating monochromator by a Ge detector. PL polarization was measured with respect to the [001] growth direction by detecting the PL intensity polarized either parallel ($I_{\parallel}$) or perpendicular ($I_{\perp}$) to the growth direction. The degree of polarization (P) was calculated using the standard equation $P=(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp})$. Time-resolved measurements were performed using femtosecond pulses from a solid state Ti:sapphire laser, with an excitation wavelength of 800 nm. Transient PL was detected by a cooled microchannel plate photomultiplier tube and a standard time-correlated photon-counting system with a time resolution better than 200 ps. ODCR experiments were done at 4 K with the aid of an Oxford optical cryostat with a magnetic field up to 5 T. The samples were placed in a cylindrical microwave cavity with a resonant frequency at 94.9 GHz. Microwave radiation was amplitude modulated by a p-i-n switch and the resulting change in the PL intensity was recorded with a lock-in technique, giving rise to the ODCR signal. The microwave power applied was about 2 mW.

In Fig. 1 we show schematic pictures of the two types of band alignment: type I (hole confinement in GaNAs, direct optical transitions) and type II (hole confinement in GaAs, indirect optical transitions). In both cases electrons are confined in GaNAs based on the well-known large bowing in the CB. Since the oscillator strength and polarization properties of the optical transitions, as well as the spatial location of the photoexcited holes, are very different for types I and II QW's (see Fig. 1), the following independent experiments can be employed to determine the band lineup.

(i) The PL decay time of the GaNAs-related near-band-edge recombination should be comparable in single epilayers and in type I QW structures, whereas significant slowing of

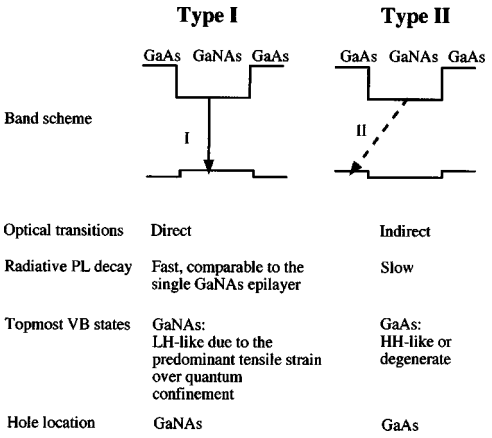

FIG. 1. Schematic band diagrams of quantum structures with types I and II band alignment. The arrows show the dominant PL recombination transitions for each structure, i.e., direct in space for the type I transitions (the solid line) and indirect in space for the type II transitions (the dashed line). LH and HH denote light and heavy holes.

the radiative decay time is expected for the spatially indirect transitions of type II QW's.[9,10]

(ii) Due to the difference in lattice constants between GaAs and GaNAs, the thin GaNAs layers in GaNAs/GaAs MQW structures are under biaxial tensile strain.[11] Because of the strain the topmost VB is light-hole-like in GaNAs QW's.[12] (For type I QW structures, the HH-LH splitting in GaNAs will be somewhat reduced due to quantum confinement effects. However, according to our results, to be discussed below, the strain contribution remains the dominant one, leading to LH character of the VB states in MQW structures). In the strain-free GaAs barriers, the LH and HH states in the VB remain degenerate for the type I structure or become predominantly HH-like for the type II band lineup due to quantum confinement.[13] Thus an analysis of the PL polarization in the QW structures can also provide information about the band alignment, because the optical transitions involving HH's or LH's are known to be different in polarization.

(iii) The spatial location (GaNAs in the case of type I or GaAs for the type II structures) of the holes participating in the radiative recombination can be directly determined by measuring the hole effective mass in, e.g., ODCR studies.

In the following we will describe the results of these experiments and will show that all of them support the type I band alignment in GaNAs/GaAs structures with a low nitrogen content.

Figure 2 compares PL decay times (dots) measured from the $GaN_{0.012}As_{0.988}$ epilayer (a) and the GaNAs/GaAs MQW structures with N composition of 1.1% [Fig. 2(b)] and 2.8% [Fig. 2(c)]. Representative PL decay curves detected at different energies are shown in the inset of Fig. 2(c), taking as an example the MQW structure with $x=2.8\%$. Similar PL transient behavior has been observed for other investigated structures. The corresponding PL spectra are also shown by solid lines for easy reference. The PL emission in all the structures has been shown[14] to be caused by recombination of localized excitons (LE's) trapped by potential fluctuations

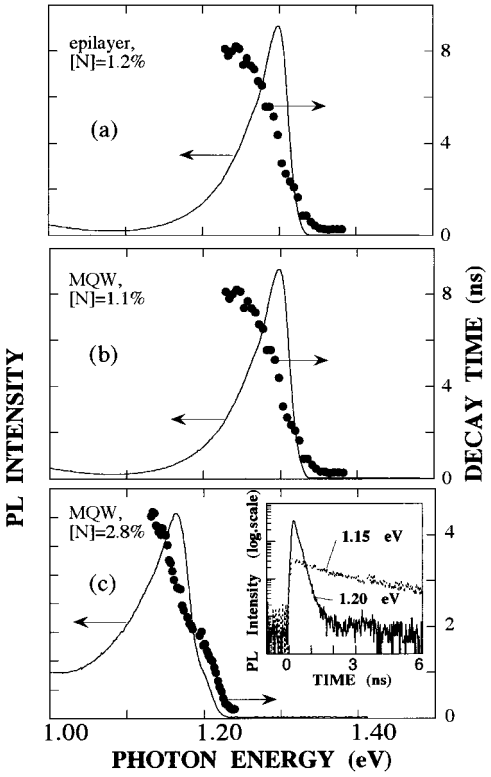

FIG. 2. Spectral dependence of the PL decay time (dots) detected at 2 K from a single $GaN_{0.012}As_{0.988}$ epilayer (a) and the GaNAs/GaAs MQW structures with N content of 1.1% (b) and 2.8% (c). The PL spectra from the same structures are also shown by solid lines, for easy reference. The inset in (c) shows representative PL decay curves measured at the specified PL energies from the GaNAs/GaAs MQW structure with $x=2.8\%$.

of the GaNAs band gap. As typically observed for LE emission,[14–17] the PL decay time increases with decreasing PL energy and saturates on the low-energy side of the PL band. This is because[15] the PL decay occurs mainly due to radiative recombination for strongly localized excitons, reflected by the rather slow exponential PL decay at low emission energies (Fig. 2). On the other hand, exciton transfer between localized states and an increasing contribution of a fast nonradiative component in the measured decay cause a decrease of the PL decay time for weakly localized excitons, evident from the appearance of the fast component of PL decay at high emission energies. Most importantly, the radiative lifetime (i.e., PL decay time on the low-energy side of the PL spectrum) in the GaNAs/GaAs MQW structures remains on the order of several nanoseconds and nearly identical to the radiative lifetime for the spatially direct PL transitions in single GaNAs epilayers. This fact provides our first piece of evidence toward the type I band alignment in the structures studied, since much longer decay times (in the range of microseconds) are expected for the spatially indirect radiative recombination in type II quantum systems.[9,10]

Further support for this conclusion comes from the polarization measurements—see Fig. 3. The GaNAs-related emission in the epilayer sample exhibits nearly 50% linear polarization along the growth direction [Fig. 3(a)] and is

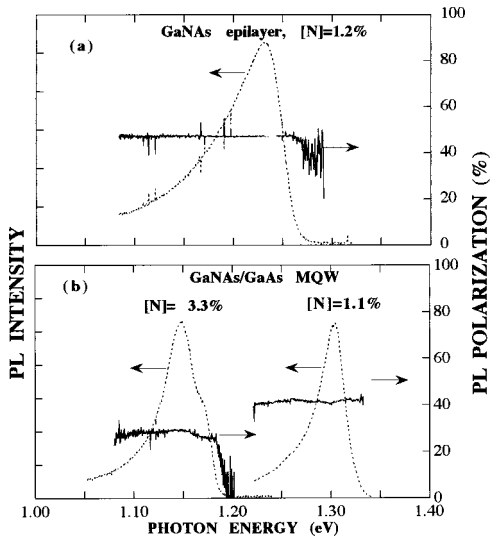

FIG. 3. Comparison of the polarization of the GaNAs-related emission measured from a single epilayer (a) and from the MQW structures (b). PL spectra of the structures investigated are shown by the dotted lines.

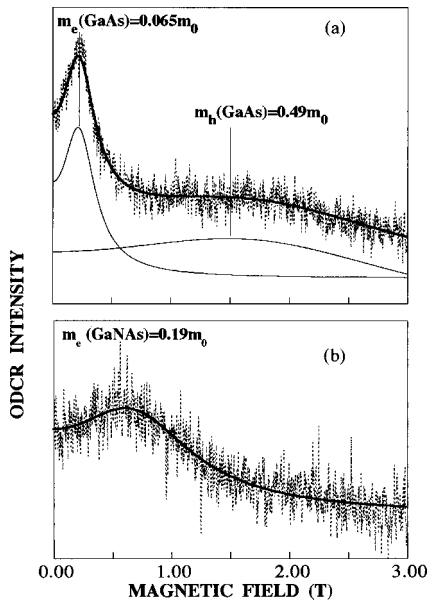

FIG. 4. The ODCR spectra detected from the $GaN_{0.019}As_{0.981}$/GaAs MQW structure under above- (a) and below- (b) barrier excitation. The dashed lines represent experimental data. The solid lines are the fitted curves according to Ref. 18, using the effective mass values specified in the figure.

independent of N content. The same preferential PL polarization remains in the MQW structures [Fig. 3(b)]; however, the degree of polarization decreases from $\approx$50% down to 20–30 % with increasing N content from 1.1% up to 3.3%.

The polarization of PL transitions due to excitonic recombination depends on the character of the hole participating in the emission. According to the selection rules, the free exciton transitions involving HH can only occur with light polarization perpendicular to the growth direction, leading to a negative value of *P*. Free-exciton transitions involving LH's occur in polarization both perpendicular and parallel to the growth direction. Thus, the observed polarization of the emission indicates that the topmost VB state in the MQW structures is LH-like, supporting the type I model. It is interesting to note that even in the 1100-Å-thick GaNAs epilayers the topmost VB state is also LH-like, most likely due to a residual biaxial tensile strain.[11,12] On the other hand, in type II MQW structures the photoexcited holes should be quantum confined in the 200-Å-thick strain-free GaAs layers. If we neglect the penetration of the hole wave function into the GaNAs layer, the polarization of the type II emission could be due to a nonzero confinement-induced splitting of the VB states in GaAs. In this case the PL will be mainly polarized perpendicular to the growth direction (e-HH transitions), like the excitonic emission in AlGaAs/GaAs QW structures.[13] The expected polarization in type II structures is obviously different from our experimental findings, where the GaNAs QW emission is strongly polarized along the growth direction [Fig. 3(b)]. Thus, the PL polarization results seem to be more consistent with a type I band lineup in GaNAs/GaAs QW's.

To further verify the type I band alignment in GaNAs/GaAs MQW structures, we have performed ODCR measurements. This is a highly sensitive magneto-optical technique providing information[18] on band structure parameters such as the effective mass of the free carriers. The ODCR spectra represent the change of PL intensity due to resonant absorption of the microwave power when the cyclotron resonance condition $\omega_c = eB/m^*$ is satisfied for either free electrons or free holes (ω_c stands for the cyclotron frequency, m^* is the effective mass of the free carriers, and B is an applied magnetic field). By fitting the shape of the ODCR spectra,[18] the effective mass of the free carriers can be determined. The ODCR spectra measured via GaNAs-related PL emission from the $GaN_{0.019}As_{0.981}$/GaAs MQW structure under above- and below-barrier excitation are presented in Fig. 4(a) and 4(b), respectively. When the energy of excitation light is higher than the GaAs band gap (i.e., above-barrier excitation) the ODCR spectrum contains two peaks corresponding to the CR of photoexcited carriers with effective masses of $0.066m_0$ and $0.47m_0$, judging from the field position of the peaks. These values are identical to the well-established values for the effective masses of free electrons and heavy holes in bulk GaAs, showing that CR occurs in the GaAs barriers. The GaAs-related ODCR peaks completely disappear when the energy of the exciting light is tuned below the GaAs band gap but still exceeds the GaNAs band gap, i.e., under resonant excitation of the GaNAs QW's [Fig. 4(b)]. Instead, a new weaker peak appears in the spectrum, proved[19] to be related to the CR of free electrons confined in GaNAs QW's with an effective mass heavier than that in GaAs.

The observation of GaAs-related CR via GaNAs-related emission under above-barrier excitation is not surprising, since the change of the recombination rate in the GaAs layers under CR conditions will affect the number of photoexcited carriers supplied to the GaNAs QW's, and, thus, the intensity of the GaNAs-related emissions. Under resonant excitation of GaNAs, the large bowing in the CB ensures that no electrons are photoexcited in GaAs and also secures confinement

of the nonequilibrium electrons in the GaNAs QW's. This leads to the disappearance of the CR from the GaAs electrons and the appearance of a CR peak from the GaNAs electrons. Most importantly, the CR peak arising from the free holes in GaAs also disappears under resonant excitation of the GaNAs QW's. This is possible only in type I structures, where resonant light absorption in the GaNAs QW's does not create free holes in the GaAs layers (Fig. 1). On the contrary, for type II structures an increase of the CR intensity for the GaAs hole relative to the CR peak from the GaNAs electron, as compared to the GaAs ODCR spectrum, would occur due to the lower electron mobility in the GaNAs layers. This is because the relative intensity of the ODCR peaks related to the photoexcited electrons and holes reflects the difference in their scattering times, under the reasonable assumption that equal number of the photoexcited electrons and holes are created due to band-to-band light absorption. The electron in GaNAs layer has a shorter scattering time (a lower mobility) than that in GaAs,[19] leading to a decrease in intensity of the electron ODCR peak under the resonant excitation of the alloy (electron in the GaNAs layer) as compared with above-barrier excitation (electron in the GaAs barrier). On the other hand, for type II structures, hole location (GaAs barriers) and thus mobility remain identical under above-barrier and resonant excitation. This should give rise to an increase in intensity of the GaAs-hole ODCR peak relative to the GaNAs-electron ODCR signal under resonant excitation conditions, which is opposite to the experimental results.

Thus the ODCR results provide another direct experimental proof that the GaNAs/GaAs structures have type I band alignment. The inability to observe CR from the GaNAs hole could be attributed to an even lower mobility such that the CR condition ($\omega\tau \geqslant 1$) is no longer fulfilled.

In summary, we have employed three independent experimental techniques, namely, time-resolved photoluminescence spectroscopy, PL polarization measurements, and optically detected cyclotron resonance studies, to determine the band alignment of GaN_xAs_{1-x}/GaAs quantum structures with N content up to 3%. We conclude that the band lineup is type I based on the following experimental results: (i) a comparable radiative decay time of the GaNAs-related emission measured from single GaNAs epilayers and the GaNAs/GaAs MQW structures; (ii) the observed PL polarization preferentially along the growth direction, typical for free-excitonic transitions involving LH's due to the strain-induced splitting of the VB states in GaNAs; and (iii) the spatial confinement of the photoexcited holes within the GaNAs layers under resonant excitation of GaNAs MQW's.

The authors would like to thank the Swedish Natural Science Research Council (NFR) for financial support. The work at UCSD was partially supported by the National Renewable Energy Laboratory (Grant No. AAD-9-18668-07).

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